potentials corresponding to those respective potentials necessary to establish current flow through the sample due to diffusional recycling of the first redox reversible species without significant interference from said second redox reversible species,

measuring current flow at said first anodic and cathodic potentials,

applying a second cathodic potential to said first or second working electrode and a second anodic potential to the other working electrode, said second cathodic and anodic potential corresponding to those respective potentials necessary to establish current flow through the sample due to diffusional recycling of the second redox-reversible-species without significant interference from the first redox reversible species,

measuring current flow at said second anodic and cathodic potentials, and

correlating the respective measured current flows to that for known concentrations of the respective diffusible redox reversible species.

2. The method of claim 1 wherein the cathodic and anodic potentials are applied to the working electrodes using a bipotentiostat.

3. The method of claim 1 wherein the redox reversible label is a metal ion complex selected from ferrocene and nitrogen-coordinated complexes of transition metal ions.

4. The method of claim 1 wherein the redox reversible label is a redox reversible organic group.

5. The method of claim 1 for measuring the concentration of two analytes in a liquid sample wherein the respective redox potentials of the first and second redox-reversible-species differ by at least 100 millivolts.

6. The method of claim 1 for measuring the concentration of one or more analytes in a liquid sample wherein current flow is measured as at least one of the anodic or cathodic potentials is held at the predetermined value and the potential of the other is swept through its predetermined value.

7. The method of claim 1 for measuring two proteinaceous analytes in a liquid sample wherein the ligand analog component of the first redox-reversible-species is a peptide comprising an epitope of a first analyte and the ligand analog component of a second redox-reversible-species is a peptide comprising an epitope of a second analyte.

8. The method of claim 7 wherein one specific binding partner is an antibody recognizing the epitope of the first analyte and the other specific binding partner is an antibody recognizing the epitope of the second analyte.

9. The method of claim 1 for measuring one analyte in a liquid sample wherein the respective ligand analog component of the first and second redox-reversible-species are different ligand analogs of a single analyte.

10. The method of claim 9 wherein the ligand analog component of the first redox reversible species is a peptide comprising a first epitope of the analyte, and the ligand analog component of the second redox-reversible-species is a peptide comprising a second epitope of the analyte, and the specific binding partners are first and second antibodies each recognizing the respective first and second epitopes.

11. A device for detecting or quantifying one or more analytes in a liquid sample, said device comprising

a sample chamber for holding the liquid sample,

at least two redox reversible species located for contact with the liquid sample in the chamber, each redox reversible species capable of diffusion in said liquid sample at least in the presence of a respective predetermined analyte, said redox-reversible species having respective redox potentials differing by at least 50 millivolts, and at least one of said redox reversible species comprising a ligand capable of binding to a specific binding partner for the analyte,

an electrode structure for contact with the liquid sample, said electrode structure including a reference electrode and working electrodes dimensioned to allow diffusional recycling of a diffusible redox reversible species in the liquid sample in contact with the electrode structure when a predetermined redox-reversible-species-dependent cathodic potential is applied to one working electrode and a predetermined redox-reversible-species-dependent anodic potential is applied to a second working electrode, said diffusional recycling of said species being sufficient to sustain a measurable current through each working electrode, and

conductors communicating with the respective electrodes for applying said anodic potential and said cathodic potential and for carrying the current conducted by the electrode.

12. The device of claim 11 wherein said chamber has a sample receiving port and is dimensioned so that it fills by capillary flow when the liquid sample is contacted with the sample receiving port.

13. The device of claim 12 wherein the redox reversible species are located for contact with the liquid sample as it flows into the chamber.

14. The device of claim 11 wherein the electrode structure comprises microarray electrodes selected from the group consisting of arrays of microdiscs, microbands or microholes.

15. The device of claim 11 wherein the electrode structure comprises interdigitated microarray electrodes.

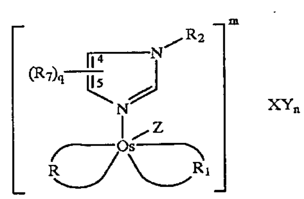
16. The device of any of claims 11 wherein at least one redox reversible species includes an osmium complex.

17. The device of claim 11 wherein at least one of the redox reversible species comprises ferrocene or a redox reversible derivative thereof.

18. The device of claim 11 wherein two redox reversible species are positioned for contact with the liquid sample as it is delivered to the chamber and each species is an osmium complex.

19. The device of claim 11 including at least one redox reversible species comprising ferrocene or a redox reversible derivative thereof and at least one redox reversible species comprising an osmium complex.

20. The device of claim 11 wherein at least one of the redox-reversible-species is an electrochemically detectable compound of the formula



wherein

R and R_1 are the same or different and are 2,2'-bipyridyl, 4,4'-disubstituted-2,2'-bipyridyl, 5-5'-disubstituted, -2,2'-bipyridyl, 1,10-phenanthrolinyl, 4,7-disubstituted-1, 10-phenanthrolinyl, or 5,6-disubstituted-1, 10-phenanthrolinyl, wherein each substituent is a methyl, ethyl, or phenyl group,

R and R_1 are coordinated to Os through their nitrogen atoms,

q is 1 or 0;

R_7 is B—$(L)_k$—$Q(CH_2)_i$—;

R_2 is hydrogen, methyl, or ethyl when q is 1, and R_2 is B—$(L)_k$—$Q(CH_2)_i$—when q is 0;

wherein in the group B—$(L)_k$—$Q(CH_2)_i$—Q is O, S, or NR_4 wherein R_4 is hydrogen, methyl or ethyl;

—L—is a divalent linker;

k is 1 or 0;

i is 1,2,3,4,5 or6; and

B is a group comprising a ligand capable of binding to a specific binding partner;

Z is chloro or bromo;

m is+1 or+2;

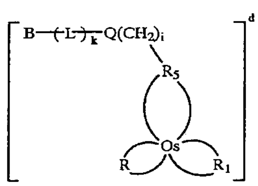
X is mono or divalent anion;

Y is a monovalent anion; and

n is 1 or zero,

provided that when X is a divalent anion, n is zero, and when m is 1, n is zero and X is not a divalent anion.

21. The device of claim 11 wherein at least one of the redox reversible species is an electrochemically detectable compound of the formula



X_xY_y

wherein

R and R_1 are the same or different and are 2,2'-bipyridyl, 4,4'-disubstituted-2,2'-bipyridyl, 5-5'-disubstituted,-2,2'-bipyridyl, 1,1 0-phenanthrolinyl, 4,7-disubstituted-1, 10-phenanthrolinyl, or 5,6-disubstituted-1,10-phenanthrolinyl, wherein each substituent is a methyl, ethyl, or phenyl group,

R_5 is 4-substituted-2,2'-bipyridyl or 4,4'-disubstituted-2,2'-bipyridyl wherein the substituent is the group B—$(L)_k$—$Q(CH_2)_i$—and the 4'-substituent is a methyl, ethyl or phenyl group;

R, R_1 and R_5 are coordinated to Os through their nitrogen atoms;

Q is O, S, or NR_4 wherein R_4 is hydrogen, methyl or ethyl;

—L—is a divalent linker;

k is 1 or 0;

i is 1, 2, 3, 4, 5 or 6;

B is a group comprising a ligand capable of binding to a specific binding partner;

d is+2 or+3;

X and Y are anions selected from monovalent anions and divalent anions sulfate, carbonate or sulfite wherein x and y are independently 0, 1, 2, or 3 so that the net charge of $X_xY_y$is−2 or−3.

22. The device of claim 11 wherein the redox reversible species have respective redox potentials differing by at least 100 millivolts.

23. The device of claim 11 wherein the redox reversible species have respective redox potentials differing at least 200 millivolts.

24. The device of claim 11 wherein the device comprises at least two electrode structures, each in the form of microarray electrodes dimensioned to enable diffusible recycling of a diffusible redox reversible species.

25. The device of claim 11 for quantifying a first analyte and a second analyte in a liquid sample, said device comprising two redox reversible species, a first redox reversible species comprising a conjugate of a ligand analog of the first analyte and a second redox reversible species comprising a conjugate of a ligand analog of the second analyte, each of said analyte analog conjugates being capable of binding competitively with its respective analyte to a specific binding partner.

26. The device of claim 25 further comprising a binding partner specific for both the first analyte and the redox reversible conjugate of the ligand analog of the first analyte and a binding partner specific for both the second analyte and the redox reversible conjugate of the ligand analog of the second analyte said specific binding partners located for contact with the liquid sample in the chamber.

27. The device of claim 11 further comprising a bipotentiostat in electrical communication with the conductors for applying a redox-reversible-species-dependent-cathodic potential to one working electrode and a redox-reversible-species-dependent-anodic potential to a second working electrode.

28. The device of claim 27 for quantifying one or more analytes in a liquid sample, said device including first and second redox reversible species, wherein the bipotentiostat is programmable, and it is programmed to apply a first cathodic potential to a first working electrode and a first anodic potential to a second working electrode, said first anodic and cathodic potentials corresponding to those potentials necessary to establish current flow through the sample due to diffusional recycling of the first redox reversible species, and wherein the bipotentiostat is programmed to apply a second cathodic potential to said first working electrode and a second anodic potential to the second working electrode, said second cathodic and anodic potentials corresponding to those potentials necessary to establish current flow through the sample due to diffusional recycling of the second redox reversible species, and means for measuring current flow through the sample at each of the first and second potentials.

29. The device of claim 27 for quantifying one or more analytes in a ligand sample, said device including first and second redox reversible species, and at least first and second electrode structures for contact with the liquid sample in the chamber, each of said electrode structures comprising a microarray of working electrodes, and a switch for changing the electrical communication of the bipotentiostat between the first and second electrode structures.

30. The device of claim 29 wherein the bipotentiostat is programmable, and it is programmed to apply a first cathodic potential to a working electrode of the first electrode structure and a first anodic potential to a second working electrode of the first electrode structure, said first anodic and cathodic potentials corresponding to those necessary to establish current flow through the sample due to diffusional recycling of the first redox reversible species, and wherein the bipotentiostat is programmed to apply a second cathodic potential to a working electrode of the second electrode structure and a second anodic potential to a second electrode of the second electrode structure, said second cathodic and anodic potential corresponding to those potentials necessary to establish current flow through the sample due to diffusional recycling of the second redox reversible species, and means for measuring current flow through the sample at each electrode structure.

31. The device of claim 11 wherein the first and second reversible species each comprise a conjugate of different ligand analogs of one analyte, each of said conjugates capable of binding competitively with said analyte to one of two independent specific binding partners for said analyte.

32. The device of claim 11 for quantifying glycosylated hemoglobin wherein at least one of the two redox reversible species comprises a conjugate of the formula

Gluc-Val-His-Leu-Thr - L - M_1

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wherein M_1 is a redox reversible label, L is a linker and Gluc-Val-His-Leu-Thr- is the N-terminal sequence of the β-chain of hemoglobin Al c.

33. The device of claim 32 wherein the redox reversible label is a metal ion complex.

34. The device of claim 32 wherein M_1 is an osmium ion complex or ferrocene.

35. The device of claim 32 wherein the other reversible redox species comprises a redox reversible conjugate of the formula

Val-His-Leu-Thr - L -M_2

wherein M_2 is a redox reversible label and L is a linker.

36. The device of claim 35 wherein the redox reversible label is a metal ion complex.

37. The device of claim 35 wherein the redox potential of M_1 and M_2 differ by at least 100 millivolts.

38. The device of claim 35 wherein the redox potential of M_1 and M_2 differ at least 200 millivolts.

39. The device of claim 35 further comprising a specific binding partner for both hemoglobin Alc and the redox reversible conjugate Gluc-Val-His-Leu-Thr-L -M_1, said specific binding partner located for contact with the sample in the chamber.

40. The device of claim 39 further comprising a specific binding partner for both hemoglobin and the redox reversible conjugate Val-His-Leu-Thr -L M_2, said specific binding partner located for contact with the sample in the chamber.

41. A kit for measuring the concentration of one or more analytes in a liquid sample, said kit comprising

at least two redox reversible species for contact with the liquid sample, each capable of diffusion in the liquid sample at least in the presence of a predetermined analyte, at least one species comprising a conjugate of a ligand analog of an analyte and a redox reversible label, said redox reversible species having respective redox potentials differing by at least 50 millivolts;

a specific binding partner for each analyte;

an electrode structure for contact with the liquid sample, said electrode structure including a reference electrode and working electrodes dimensioned to allow diffusional recycling of diffusible redox reversible species in the sample when a predetermined redox-reversible-species-dependent-cathodic potential is applied to one working electrode and a predetermined redox-reversible-species-dependent-anodic potential is applied to the second working electrode, said diffusional recycling of said species means sufficient to sustain a measurable current through the sample; and

conductors communicating with the respective electrodes for applying said anodic potential and said cathodic potential and for carrying the current conducted by the electrodes.

42. The kit of claim 41 wherein the electrode structure comprises microarray electrodes selected from the group consisting of arrays of microdiscs, microbands, or microholes.

43. The kit of claim 41 wherein the electrode structure comprises interdigitated microarray electrodes.

44. The kit of claim 41 wherein the redox reversible species are mixed as a composition for contact with the liquid sample.

45. The kit of claim 41 wherein the redox reversible label of at least one redox reversible species comprises an osmium complex.

46. The kit of claim 41 wherein the redox reversible species have respective redox potentials differing by at least 100 millivolts.

47. The kit of claim 41 wherein the redox reversible species have respective redox potentials differing by at least 200 millivolts.

* * * * *

48. A method for measuring in a sample the concentration of a first redox reversible species in the presence of a second redox reversible species, wherein said first and second redox reversible species have redox potentials differing by at least 50 millivolts, said method comprising

electrochemically determining the concentration of each of said redox-reversible species in the liquid sample by

contacting said sample with an electrode structure including a reference electrode and at least first and second working electrodes dimensioned to allow diffusional recycling of the redox reversible species in the sample when a predetermined redox-reversible-species-dependent cathodic potential is applied to one working electrode and a predetermined redox-reversible-species-dependent anodic potential is applied to a second working electrode, said diffusional recycling of said species being sufficient to sustain a measurable current through said sample,

applying a first cathodic potential to the first working electrode and a first anodic potential to the second working electrode, said first cathodic and anodic potentials corresponding to those respective potentials necessary to establish current flow through the sample due to diffusional recycling of the first redox reversible species without significant interference from said second redox reversible species,

measuring current flow at said first anodic and cathodic potentials,

applying a second cathodic potential to said first or second working electrode and a second anodic potential to the other working electrode, said second cathodic and anodic potential corresponding to those respective potentials necessary to establish current flow through the sample due to diffusional recycling of the second redox-reversible-species without significant interference from the first redox reversible species,

measuring current flow at said second anodic and cathodic potentials, and

correlating the respective measured current flows to that for known concentrations of the respective diffusible redox reversible species.

49. The method of claim 48 wherein the cathodic and anodic potentials are applied to the working electrodes using a bipotentiostat.

50. The method of claim 48 wherein the redox reversible species includes a metal ion complex selected from ferrocene and nitrogen-coordinated complexes of transition metal ions.

51. The method of claim 48 wherein the redox reversible species includes is a redox reversible organic group.

52. The method of claim 48 wherein the respective redox potentials of the first and second redox-reversible-species differ by at least 100 millivolts.

53. The method of claim 48 wherein current flow is measured as at least one of the anodic or cathodic potentials is held at the predetermined value and the potential of the other is swept through its predetermined value.

54. Method of determining the amount or concentration of a plurality of diffusible redox-reversible species in a solution, comprising:

providing an electrochemical measurement cell comprising at least two working electrodes and a reference electrode, said working electrodes so configured and arranged that redox recycling of diffusible redox-reversible species takes place between the working electrodes when appropriate potentials are applied,

contacting the solution with the electrodes in the measurement cell,

applying potentials to the working electrodes such that a current through the cell is generated as a result of redox recycling of at least one diffusible redox-reversible species,

applying potentials to the working electrodes such that a current through the cell is generated as a result of redox recycling of a second diffusible redox-reversible species

wherein said diffusible redox-reversible species have equilibrium potentials that differ by more than about 50 mV.

55. Method of claimed 54 where the current generated correlates to the concentration of one or more diffusible redox recycling species.

56. Method of claim 54 where at least one of the responses are correlated with at least one analyte concentration

57. Method of claim 54 where the measured concentration of one species is corrected by the response of another species.

58. Method of determining the relative diffusion coefficients of a plurality of diffusible redox-reversible species in a solution, comprising:

providing an electrochemical measurement cell comprising at least two working electrodes and a reference electrode, said working electrodes so configured and arranged that redox recycling of diffusible redox-reversible species takes place between the working electrodes when appropriate potentials are applied,

contacting the solution with the electrodes in the measurement cell,

applying potentials to the working electrodes such that a current through the cell is generated as a result of redox recycling of at least one of the diffusible redox-reversible species,

applying potentials to the working electrodes such that a current through the cell is generated as a result of redox recycling of a second diffusible redox-reversible species

wherein said diffusible redox-reversible species have equilibrium potentials that differ by more than about 50 mV.

59. A method for measuring the concentration of an analyte in a liquid sample, said method comprising:

reacting a compound with said analyte to generate a first redox reversible species in said liquid in the presence of a second redox reversible species, wherein said first and second redox reversible species have redox potentials differing by at least 50 millivolts

electrochemically determining the concentration of each of said redox-reversible species in the liquid sample by

contacting said sample with an electrode structure including a reference electrode and at least first and second working electrodes dimensioned to allow diffusional recycling of the redox reversible species in the sample when a predetermined redox-reversible-species-dependent cathodic potential is applied to one working electrode and a predetermined redox-reversible-species-dependent anodic potential is applied to a second working electrode, said diffusional recycling of said species being sufficient to sustain a measurable current through said sample,

applying a first cathodic potential to the first working electrode and a first anodic potential to the second working electrode, said first cathodic and anodic potentials corresponding to those respective potentials necessary to establish current flow through the sample due to diffusional recycling of the first redox reversible species without significant interference from said second redox reversible species,

measuring current flow at said first anodic and cathodic potentials,

applying a second cathodic potential to said first or second working electrode and a second anodic potential to the other working electrode, said second cathodic and anodic potential corresponding to those respective potentials necessary to establish current flow through the sample due to diffusional recycling of the second redox-reversible-species without significant interference from the first redox reversible species,

measuring current flow at said second anodic and cathodic potentials, and

correlating the respective measured current flows to that for known concentrations of the respective diffusible redox reversible species.